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Technical University of Berlin, Germany, 5 April 2002–1 May 2002

Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of “dreams” for organic chemists. Our main research interest is the elucidation of the resemblance and difference in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry. Organic synthesis mediated by biocatalysts is also studied.

Research Activities (Year 2002)

Presentations

Chalcogenation reaction of kinetically stabilized doubly bonded systems between heavier group 15 elements, Sasamori T, Takeda N, Tokitoh N, 20th International Symposium on the Organic Chemistry of Sulfur, 14 - 19 July, Flagstaff, USA.

New aspects in the chemistry of silaarenes, Tokitoh N, The 13th International Symposium on Organosilicon Chemistry, 25 - 30 August, Guanajuato, Mexico.

Synthesis, structure, and reactions of the first platinum complexes bearing a disulfur and diselenium ligand, Nagata K, Takeda N, Tokitoh N, 49th Symposium on Organometallic Chemistry, Japan, 12 - 13 September, Kobe.

Synthesis, structure, and reactivities of the first stable

germabenzene, Nakata N, Takeda N, Tokitoh N, 16th Symposium on Fundamental Organic Chemistry, 3 - 5 October, Tokyo.

Grants

Tokitoh N, Studies on the synthesis, structures, properties, and functions of novel aromatic compounds containing heavier group 14 elements, Grant-in-Aid for Scientific Research (A), 1 April 2002 - 31 March 2005.

Tokitoh N, Synthesis of dynamic complexes containing heteroatoms by taking advantage of kinetic stabilization, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2002 - 31 March 2006.

Takeda N, Synthesis of novel multiple-bond species of silicon by taking advantage of silylene-isocyanide complexes and

Synthesis and properties of the first stable germabenzene

In recent decades, much attention has been focused on the chemistry of $[4n+2]\pi$ -electron ring systems containing heavier group 14 elements. However, no synthesis and isolation of these compounds as stable molecules had been reported until quite recently due to their extremely high reactivity. We have recently succeeded in the synthesis and characterization of the first stable silabenzene, 2-silanaphthalene, 9-silaanthracene, and 2-germanaphthalene by taking advantage of an efficient steric protection group, Tbt group (*vide infra*). These successful results naturally prompted us to extend this method to the synthesis of a germabenzene, the most fundamental germaaromatic compound having a simple 6 π -electron ring system.

The first stable germabenzene **1** was successfully synthesized by the reaction of the corresponding chlorogermene **2** with $\text{LiN}(i\text{-Pr})_2$ in THF. Although the structural and spectroscopic data and theoretical calculations showed that **1** had aromaticity, in the reactions with MeOH, MesCNO, styrene, phenylacetylene, and 2,3-dimethyl-1,3-butadiene, **1** underwent 1,2- and/or 1,4- addition to the 1-germabuta-1,3-diene moiety reflecting the extremely high reactivity of the Ge–C double bond.



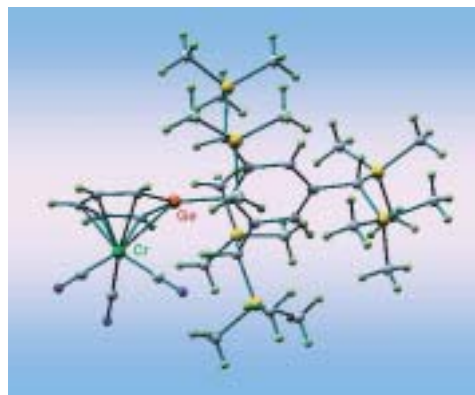
The reactions of **1** with $\text{M}(\text{CH}_3\text{CN})_3(\text{CO})_3$ [M = Cr, Mo] gave the corresponding η^6 -germabenzene complexes of group 6 metals **3**. These results are very interesting because **3** is the first η^6 -germabenzene complexes and these reactions are the first examples showing the aromatic character of germabenzene from the viewpoint of reactivity.

their properties, Grant-in-Aid for Young Scientists (B), 1 Apr 2001 - 31 March 2003.

Awards

Hirano T, Best Poster Presentation Award, Analysis of carbon, hydrogen, and nitrogen contents in silicon-containing compounds using YANACO CHN-CORDER MT-5, The Association of Organic Micro-analysis, 10 May 2002.

Sasamori T, Takeda N, Tokitoh N, The Best Article of the Month, Syntheses, structures and properties of kinetically stabilized distibenes and dibismuthenes, novel doubly bonded sys-



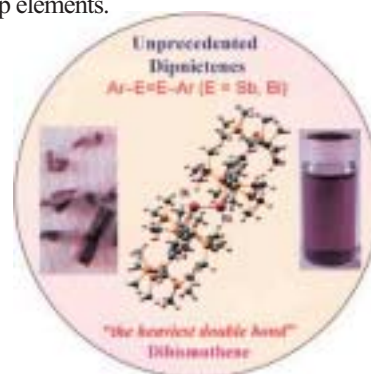
X-ray Structural Analysis of **3**

Synthesis, structures, and properties of novel doubly bonded systems between heavier group 15 elements

Recently, there has been much interest in compounds with a double bond between heavier group 15 elements.

The first stable distibenes and dibismuthenes were successfully synthesized by taking advantage of efficient steric protection groups, Tbt and Bbt groups. The crystallographic analysis, and spectroscopic studies of these stable dipnictenes and theoretical calculations of model compounds led to the systematic comparison of structural parameters and physical properties for all homonuclear doubly bonded systems between heavier group 15 elements.

In addition, condensation of Mes^*PH_2 (Mes = 2,4,6-*tert*-butylphenyl) with BbtBiBr_2 using 1,8-diazabicyclo[5.4.0]undec-7-ene as a base afforded the first stable phosphabismuthene $\text{Mes}^*\text{P}=\text{BiBbt}$, which is also the first stable double-bond compound between the third and sixth row main group elements.



tems between heavier group 15 elements, The Chemical Society of Japan, 25 September 2002.

Shinohara A, Symposium Poster Award, 7th Symposium of the Society of Silicon Chemistry, Japan, Synthesis and properties of kinetically stabilized 1-silanaphthalene, the Society of Silicon Chemistry, Japan, 16 November 2002.

Yamanaka R, Best Presentation Award, The 6th Japanese Symposium on the Chemistry of Biocatalysis, Light-mediated regulation of asymmetric reduction of ketones, Group Biocatalyst Chemistry Japan, 12 December 2002.